

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 31-07-2007		2. REPORT TYPE Book Chapter		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Microbiologically Influenced Corrosion in Military Environments				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 0601153N	
6. AUTHOR(S) Jason S. Lee, Richard I. Ray, Brenda J.				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 73-5052-14-5	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Oceanography Division Stennis Space Center, MS 39529-5004				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/BC/7303-04-1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy St. Arlington, VA 22217-5660				10. SPONSOR/MONITOR'S ACRONYM(S) ONR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT MICROBIOLOGICALLY INFLUENCED CORROSION (MIC) designates corrosion due to the presence and activities of microorganisms. Microorganisms can accelerate rates of partial reactions in corrosion processes and/or shift the mechanism for corrosion processes and/or shift the mechanism for corrosion (Ref 1). Most laboratory and field MIC studies have focused on bacterial involvement; however, other single-celled organisms, including fungi, can influence corrosion. This article focuses on MIC of military assets and is divided into atmospheric, hydrocarbon and water immersed, and buried environments. Individual mechanisms for MIC are discussed for specific examples. More general discussions of MIC are found in the articles "Microbiologically Influenced Corrosion" and Microbiologically Influenced Corrosion Testing" in ASM Handbook, Volume 13A. 2003.					
15. SUBJECT TERMS microorganisms; metals; atmospheric corrosion; immersion					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 10	19a. NAME OF RESPONSIBLE PERSON Jason S. Lee
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 228-688-4494

ASM Handbook®

Volume 13C Corrosion: Environments and Industries

Prepared under the direction of the
ASM International Handbook Committee

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Microbiologically Influenced Corrosion in Military Environments

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MICROBIOLOGICALLY INFLUENCED CORROSION (MIC) designates corrosion due to the presence and activities of microorganisms. Microorganisms can accelerate rates of partial reactions in corrosion processes and/or shift the mechanism for corrosion (Ref 1). Most laboratory and field MIC studies have focused on bacterial involvement; however, other single-celled organisms, including fungi, can influence corrosion. This article focuses on MIC of military assets and is divided into atmospheric, hydrocarbon and water immersed, and buried environments. Individual mechanisms for MIC are discussed for specific examples. More general discussions of MIC are found in the articles "Microbiologically Influenced Corrosion" and "Microbiologically Influenced Corrosion Testing" in *ASM Handbook*, Volume 13A, 2003.

General Information about Microorganisms

Liquid water is needed for all forms of life, and availability of water influences the distribution and growth of microorganisms. Water availability can be expressed as water activity (a_w) with values ranging from 0 to 1. Microbial growth has been documented over a range of water activities from 0.60 to 0.998. Microorganisms can grow in the temperature range in which water exists as a liquid, approximately 0 to 100 °C (32 to 212 °F). Microorganisms can grow over a range of 10 pH units or more (Ref 2). Many microorganisms can withstand hundred-fold or greater variations in pressure. The highest pressure found in the ocean is slightly inhibitory to growth of many microorganisms. Heavy metal concentrations as low as 10^{-8} M can inhibit the growth of some microorganisms, while others may continue to grow at concentrations of a millionfold or greater. Microbial species show thousandfold differences in susceptibility to irradiation (Ref 3).

Microorganisms also require nutrients and electron acceptors. All organisms require carbon, nitrogen, phosphorus, and sulfur, in addition

to trace elements. Microorganisms can use many organic and inorganic materials as sources of nutrients and energy (Ref 2). Organisms that require oxygen as the terminal electron acceptor in respiration are referred to as aerobes. Anaerobes grow in the absence of oxygen and can use a variety of terminal electron acceptors, including sulfate, nitrate, Fe^{+3} , Mn^{+4} , and others. Organisms that can use oxygen in addition to alternate electron acceptors are known as facultative anaerobes. Microbial nutrition and respiration are coupled and adapted to environmental conditions. Additionally, microorganisms living in consortia can produce growth conditions, nutrients, and electron acceptors not available in the bulk environment.

Atmospheric Corrosion

Because fungi are the most desiccant-resistant microorganisms and can remain active down to $a_w = 0.60$ (Ref 4), they are the microorganisms most frequently involved in atmospheric MIC. Most fungi are aerobes and are found only in aerobic habitats. Fungi are nonphotosynthetic organisms, having a vegetative structure known as a hyphae, the outgrowth of a single microscopic reproductive cell or spore. A mass of threadlike hyphae make up a mycelium. Mycelia are capable of almost indefinite growth in the presence of adequate moisture and nutrients so that fungi often reach macroscopic dimensions. Spores, the nonvegetative dormant stage, can survive long periods of unfavorable growth conditions (drought and starvation). When conditions for growth are favorable, spores germinate.

Biodeterioration due to fungi has been documented for the following nonmetallic military assets: celluloses (paper, composition board, and wood); photographic film; polyvinyl chloride films; sonar diaphragm coatings; map coatings; paints; textiles (cotton and wool); vinyl jackets; leather shoes; feathers and down; natural and synthetic rubber; optical instruments; mechanical, electronic, and electric equipment

(radar, radio, flight instruments, wire strain gages, and helicopter rotors); hammocks; tape; thermal insulation; and building materials. Fungi cause corrosion in atmospheric environments by: acid production, indirect dissolution of coatings, or direct degradation of coatings. Direct degradation is related to derivation of nutrients. Fungi assimilate organic material and produce organic acids including oxalic, lactic, formic, acetic, and citric (Ref 4).

Researchers isolated the following fungal genera from polyurethane-coated 2024 aluminum helicopter interiors (Ref 5): *Pestalotia*, *Trichoderma*, *Epicoecium*, *Phoma*, *Stemphylium*, *Hormoconis* (also known as *Cladosporium*), *Penicillium*, and *Aureobasidium* (Fig. 1). Several genera, including *Aureobasidium*, penetrated the polyurethane topcoat but not the chromate primer. The result was disbonding of the topcoat

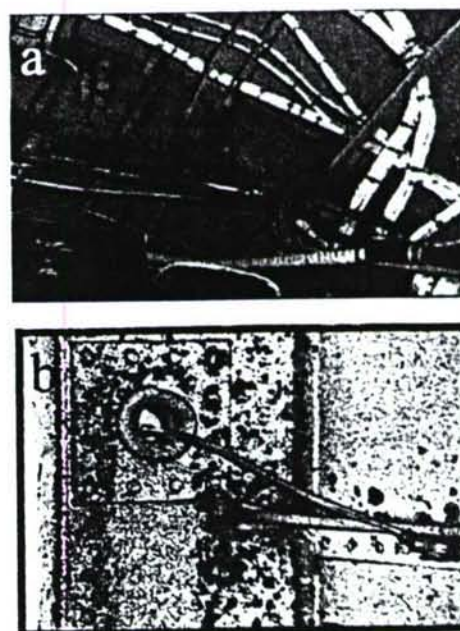


Fig. 1 Interiors of H-53 helicopter showing fungal growth on polyurethane painted surfaces. (a) Overview; (b) Detail of cable penetration

(Fig. 2), with no corrosion of the base metal as long as the primer was intact. The biocidal properties of the chromate primer (Ref 6) were documented. None of the isolates in the study detailed in Ref 5 degraded the polyurethane coating directly as a sole source of nutrients; however, all grew on hydraulic fluid that accumulated on painted interiors during routine operations. Glossy finish polyurethane was colonized more rapidly than the same formulation with a flat finish. Aged paint fouled more rapidly than did new coatings. Laboratory tests demonstrated that in the presence of hydraulic fluid, all of the isolates caused localized corrosion of bare 2024 aluminum. It was demonstrated (Ref 5) that performance specification (MIL PRF 85570) for cleaning painted aircraft interiors is effective in removing fungal spores but does not kill fungal cells embedded in the paint. Fungal regrowth was observed within days of cleaning.

Numerous reports document fungal degradation of coatings and, in some cases, corrosion of the underlying metal (Ref 7-9) in atmospheric exposures. It was reported (Ref 10) that ship cargo holds coated with chlorinated rubber and carrying dry cereals and woods were severely corroded within months. Heavy pitting and reduced thickness of the steel plate were observed. Corrosion products were populated with viable fungi. It was demonstrated (Ref 10) that the fungi derived nutrients from degradation of protective coatings in addition to the cargo. Corrosion resulted from acidic metabolic by-products. Deterioration of the epoxy resin coating of ship holds filled with molasses, fatty oils, and other fluid cargoes was reported (Ref 11). Others (Ref 12) studied direct microbial degradation of coatings, such as Buna-N (a polymer of acrylonitrile and butadiene); polyurethane (a carbamate polymer); and a polysulfide. They found that both bacteria and fungi could degrade these coatings. Pitting of the underlying metal coincided with blisters and the presence of microorganisms. It was demonstrated (Ref 13) that malfunctioning of M483 155-mm howitzer shells stored in humid environments was directly related to fungal degradation of the lubricating grease used to facilitate the screw connection between the base and the body of the shell.

Indirect dissolution of protective greases by fungi was investigated (Ref 14). Protective greases are used to provide corrosion protection for seven-strand carbon steel cable used as wire rope and as highlines. Each cable is made of six strands wrapped around a central core. When cable is used as rope or highline, the cable is coated with thick maintenance grease, threaded onto wooden spools (Fig. 3a-c), and wrapped in brown paper and black plastic. The maintenance grease is applied to the cable to provide corrosion protection. Wire rope is stored on wooden spools for weeks to months before being used. In an investigation of localized corrosion on wire rope stored on wooden spools, fungal growth was observed on interiors of some wooden spools stored outdoors. Corrosion was most severe on wraps of wire in direct contact with the wooden

spool flanges. *Aspergillus niger* and *Penicillium* sp. were isolated from wooden spool flanges (Fig. 4). Fungal isolates could not grow on the protective grease as the sole nutrient source. The isolates grew on wood and produced copious amounts of acids and CO_2 . In all cases, localized corrosion was observed in areas where acidic condensate dissolved the maintenance grease and exposed bare areas of carbon steel.

Researchers (Ref 15) determined that 80% of lubricants used for protecting materials were contaminated with 38 biological agents (21 fungi

and 17 bacteria) during storage and use, independent of climate or relative humidity. They identified the following species as those most frequently isolated from lubricating oils: *Aspergillus versicolor*, *Penicillium chrysogenum*, *Penicillium verrucosum*, *Scopulariopsis brevicaulis*, *Bacillus subtilis*, and *Bacillus pumilis*. Microorganisms isolated from one particular lubricant could not always grow vigorously on others. Microbial growth in lubricants was accompanied by changes in color, turbidity, acid number, and viscosity. Acid number refers to the acid or base

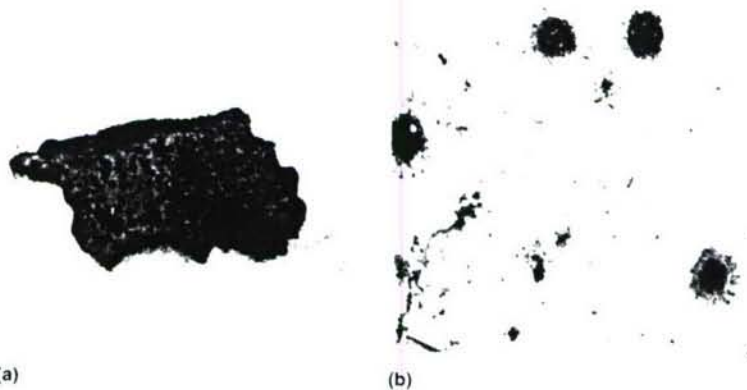


Fig. 2 A piece of disbonded polyurethane paint showing growth of fungi. (a) Top surface, (b) Underside showing that fungi had penetrated the coating

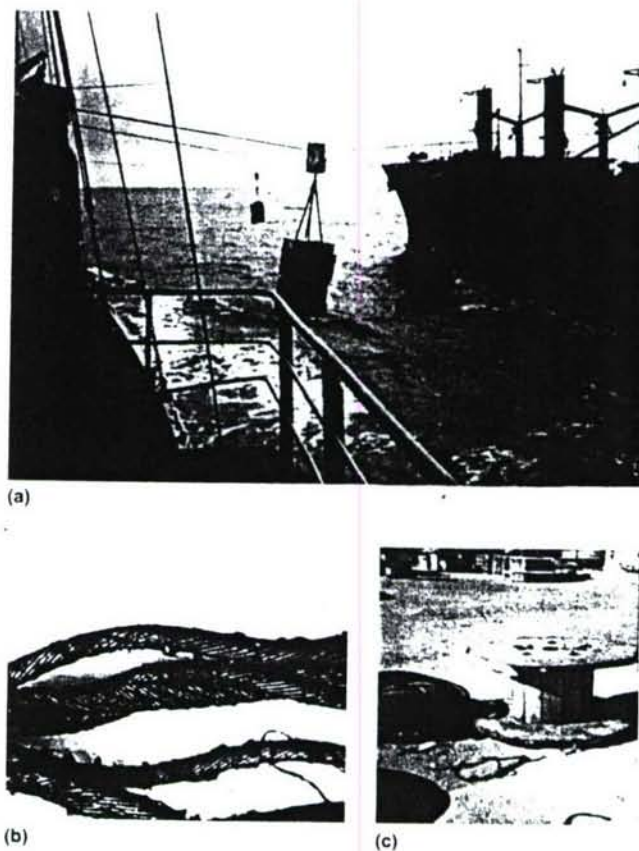


Fig. 3 Carbon steel wire rope. (a) Carbon steel highline being used to transfer equipment between ships at sea. (b) Seven-strand carbon steel wire rope with maintenance grease. (c) Typical wooden spool used to store wire rope

composition of lubricating oils and is also referred to as corrosion number. Biocides, including 4-caproyl, have been evaluated as additives to protect lubricants from mold formation. Biocides have limited lifetimes and limited effectiveness (Ref 16).

Metals Exposed to Hydrocarbon Fuels

One of the most persistent corrosion problems throughout the military is the result of microbial contamination and decomposition of hydrocarbon fuels during fuel transportation, storage, and use. Microbial interaction with hydrocarbon fuels is limited to water availability. Water is sparingly soluble in hydrocarbons. Therefore, microbial growth in hydrocarbons is concentrated at oil/water interfaces, emulsified water, and in separate water phases. The volume of water required for microbial growth in hydrocarbon fuels is extremely small. Because water is a product of the microbial mineralization of organic substrates, it is possible for microbial mineralization of fuel to generate a water phase for further proliferation. For example, *Hormoconis resinae*, the kerosene fungus, grew in 80 mg water per liter of kerosene, and after four weeks' incubation, the concentration of water increased more than tenfold (Ref 17).

The first step in microbial decomposition of hydrocarbons is an aerobic process that requires molecular oxygen. Researchers (Ref 18) compared degradation of hydrocarbons by bacteria and fungi. Bacteria showed decreasing abilities to degrade alkanes with increasing chain length. Filamentous fungi did not exhibit a preference for specific chain lengths. The first products of microbial oxidation of hydrocarbons are alcohols, aldehydes, and aliphatic acids.

An increase in the corrosivity of jet fuel (JP4) stored underground in unlined rock caverns in

Sweden caused by sulfate-reducing bacteria (SRB) was documented (Ref 19). Several authors have documented the problem of MIC in aircraft fuel tanks. It was proposed (Ref 20, 21) that microorganisms influenced corrosion of aluminum fuel tanks by:

- Removing corrosion inhibitors, including phosphate and nitrate, from the medium
- Producing corrosive metabolites
- Establishing microcenters for galvanic activity, including oxygen concentration cells
- Removing electrons directly from the surface of the metals

Several investigators reported a decrease in bulk fuel pH due to metabolites produced during growth of fungi (Ref 21–25). One researcher (Ref 24) demonstrated a correlation between growth of *Cladosporium (Hormoconis)* and pH at fuel/water interfaces and measured pH values between 4.0 and 5.0 in the fuel. Fungal-influenced corrosion has been reported for carbon steel and aluminum alloys exposed to hydrocarbon fuels. Another investigator (Ref 22) demonstrated metal ion binding by fungal mycelia, resulting in metal ion concentration cells on aluminum surfaces. It was reported (Ref 24) that corrosivity increased with contact time due to accumulation of metabolites under microbial colonies attached to metal surfaces. Others (Ref 25) demonstrated that the metabolic products enhanced aqueous phase aggressiveness even after the life cycle of *Cladosporium (Hormoconis)* was completed.

Microbiologically influenced corrosion has been identified in engines, holding tanks, skiffs, and oily waste tanks on surface ships due to microorganisms growing in water contaminated hydrocarbons. One study (Ref 26) determined that ship engine malfunction and corrosion were associated with MIC. The researchers identified both bacteria and fungi growing in engine lubricants and attributed the problem to a combination of mechanisms, including depletion of protective additives, acid production, and sulfide production. Progressive changes in the formulations of lubricating oils have introduced nitrogen, phosphorus, and sulfur which provide required nutrients for microbial growth. The current trend to produce environmentally benign engine oils means that the resulting formulations are more readily biodegraded. Slow-speed marine engines are at risk because they run for long periods of time at constant temperatures (37 to 55 °C, or 99 to 131 °F) conducive to microbial growth. Oil additives that encourage microbial growth include (Ref 26):

Metal soaps, e.g., barium sulphonates
Polyalkenyl succinimides
High-molecular-weight carboxylic acids
Metal dithiophosphates
Polyorganosiloxanes
Hindered phenols, e.g., 2,6-di-tert-butyl-4-methyl phenol
Aromatic amines-phenyl B naphthylamine
Alkyl phosphates
Alkyl-Aryl phosphates, e.g., tricresyl phosphate

Immersion

Immersion environments are those in which the surface is boldly exposed to an aqueous environment, in contrast to the previous examples in which water was the limiting factor for microbial growth. The most important factor controlling the distribution of microorganisms in immersion environments is the availability of nutrients. For example, organic nutrients and bacteria are most abundant in the upper layers of oceans, and both decrease with depth (Ref 27). Microbial biofilms develop on all surfaces in contact with aqueous environments (Ref 28). Chemical and electrochemical characteristics of the substratum influence biofilm formation rate and cell distribution during the first hours of exposure. Electrolyte concentration, pH, organic, and inorganic ions also affect microbial settlement. Biofilms produce an environment at the biofilm-surface interface that is radically different from that of the bulk medium in terms of pH, dissolved oxygen, and inorganic and organic species. In some cases, the presence of localized microbial colonies can cause differential aeration cells, metal concentrations cells, and under-deposit corrosion. In addition, reactions within biofilms can control corrosion rates and mechanisms. Reactions are usually localized and can include:

- Sulfide production
- Acid production
- Ammonia production
- Metal deposition
- Metal oxidation/reduction
- Gas production

Many of the problems of MIC of military assets exposed to aqueous environments are directly related to an operational mode that includes periods of stagnation. Heat exchangers, fire protection systems, holding tanks, and transfer lines are exposed to flow/no-flow cycles. The following statements are applicable for distilled/demineralized, fresh, estuarine, and marine waters. During stagnation, naturally occurring microorganisms form a biofilm, and aerobic microorganisms use the dissolved oxygen as the terminal electron acceptor. If the rate of respiration is faster than the rate of oxygen diffusion through the biofilm, the metal/biofilm interface becomes anaerobic, allowing anaerobic bacteria to produce corrosive metabolites, including acids and sulfides. The amount of sulfide that can be produced within a biofilm depends on the sulfate concentration and the numbers and activities of SRB. Seawater contains approximately 2 g/L of sulfate and a population of SRB whose numbers vary with nutrient concentration. Most sulfide films are not tenacious and are easily removed by turbulence. Introduction of flowing oxygenated water causes oxidation and/or disruption of surface deposits formed under stagnant conditions.

Copper alloys have a long history of successful application in seawater piping systems

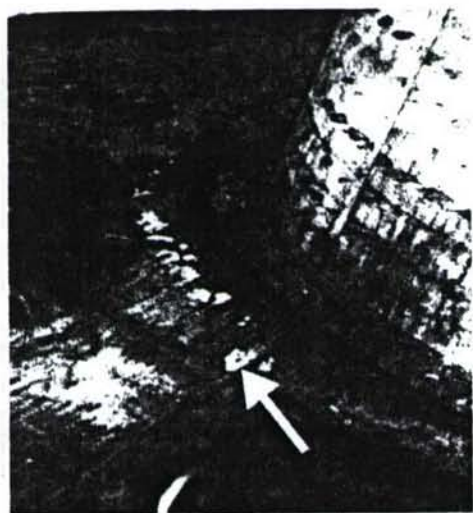


Fig. 4 Fungi (white spots) growing on inside flange of wooden spoon.

due to their corrosion resistance, antifouling properties, and mechanical properties. The corrosion resistance of copper in seawater is attributable to the formation of a protective film that is predominantly cuprous oxide, irrespective of alloy composition (Ref 29). Copper ions and electrons pass through the film. In seawater, copper ions dissolve and precipitate as $\text{Cu}_2(\text{OH})_3\text{Cl}$ (Ref 30). Copper seawater piping systems are often exposed to polluted harbor water containing sulfides. In the presence of sulfides, copper ions migrate through the layer, react with sulfide, and produce a thick black scale. Failure of copper-nickel pipes in estuarine and seawaters can be associated with waterborne sulfides that stimulate pitting and stress corrosion cracking (Ref 31–34). 90Cu-10Ni suffered accelerated corrosion attack in seawater containing 0.01 ppm sulfide after a one day exposure (Ref 35). Galvanic relationships between normally compatible copper piping and fitting alloys become incompatible after exposure to sulfide-containing seawater (Ref 33).

Sulfides produced within biofilms have the same effect as waterborne sulfides on copper alloys. Alloying additions of nickel and iron into the highly defective p-type Cu_2O corrosion product film alters the structure (Ref 29) and results in a film that possesses low electronic and ionic conductivity. In an attempt to prevent sulfide-induced corrosion of copper-nickel piping, FeSO_4 treatments were evaluated. Corrosion of FeSO_4 -treated pipes was compared with untreated pipes that had been cleaned according to military specifications (Ref 36). Batch FeSO_4 treatments did not result in a persistent increase in surface-bound iron. The authors found that the dissolved iron concentration in most harbor waters exceeded the amount of iron in the recommended batch FeSO_4 treatments. Ferrous sulfate (0.10 mg/L ferrous ion) treatments for 90Cu-10Ni and 70Cu-30Ni alloys were evaluated (Ref 37). Neither pretreatment before sulfide exposure nor intermittent treatment during sulfide exposure significantly reduced sulfide attack on either alloy. However, continuous treatment eliminated the attack on both alloys because the FeSO_4 removed sulfides from solution.

Nickel Alloys. Nickel 201, sometimes used for heat exchangers with distilled water, is vulnerable to microbiologically produced acids (Ref 38). The Ni-Cu alloys are used in seawater under conditions including high velocity (propeller shafts, propellers, pump impellers, pump shafts, and condensers), where resistance to cavitation and impingement is required. Under turbulent and erosive conditions, nickel-copper alloys are superior to predominantly copper alloys because the protective surface film remains intact. Nickel alloys are used extensively in highly aerated, high-velocity seawater applications. The formation of the protective film on nickel is aided by the presence of iron, aluminum, and silicon. However, under stagnant seawater conditions, nickel-copper alloys are susceptible to pitting and crevice corrosion

attack where chlorides penetrate the passive film (Ref 39). Sulfides produced by SRB cause either a modification or breakdown of the oxide layer and dealloying (Ref 40). Another report (Ref 41) indicated that predominantly nickel alloys were susceptible to underdeposit corrosion and oxygen concentration cells. Other studies (Ref 42, 43) demonstrated pitting and denickelification of nickel-copper tubes exposed in Arabian Gulf seawater with deposits of SRB.

Stainless Steels. The corrosion resistance of stainless steel is due to the formation of a thin passive chromium-iron oxide film. Crevice corrosion is the most problematic issue affecting the performance of stainless steels in seawater. Investigators (Ref 44) studied crevice corrosion of stainless steel beneath dead barnacles and proposed the following scenario:

- Decomposition of the barnacle by aerobic bacteria, including *Thiobacillus*, reduces pH within the barnacle shell.
- The acid penetrates the shell base and initiates a corrosion cell between the crevice area and the exposed SS substratum.
- Crevice corrosion initiates near the edge of the shell base and propagates inward.

Crevice corrosion is exacerbated in warm natural seawater where biofilms form rapidly. Pit propagation under barnacles is assisted by poor water circulation.

Several investigators (Ref 45–52) have documented the tendency for biofilms to cause a noble shift, or an ennoblement, in open-circuit potential of passive alloys exposed in marine environments. Alloys tested include, but are not limited to: UNS S30400, S30403, S31600, S31603, S31703, S31803, N08904, N08367, S44660, S20910, S44735, N10276, and R50250. The practical importance of ennoblement is increased probability of localized corrosion as E_{corr} approaches the pitting potential (E_{pit}) for stainless steels vulnerable to crevice corrosion, especially types 304 (UNS S30400) and 316 (UNS S31600). Investigators (Refs 53, 54) concluded that biofilms increased the propagation rate of crevice corrosion for UNS S31603, S31725 and N08904 by 1 to 3 orders of magnitude. They attributed ennoblement to an increase in kinetics of the cathodic reaction by the biofilms. Others (Ref 55, 56) demonstrated that ennoblement of electrochemical potential in the presence of a biofilm could be reconciled without reference to modified oxygen reduction mechanisms and without enhancement of cathodic processes. They concluded that the biofilm does not directly affect oxygen reduction near the equilibrium potential and far from the oxygen diffusion limiting current. They further concluded that H_2O_2 and manganese oxides did not play a direct role in the oxygen reduction process at potentials $> 300\text{mV}_{\text{SCE}}$. Instead, they demonstrated that anodic oxidation of organic material in biofilms produced currents corresponding to passive currents or higher. Oxidation of organic material affects the value of the

corrosion potential and lowers the pH at the surface.

One of the most common forms of MIC attack in austenitic stainless steel is pitting at or adjacent to welds. The following observations were made for MIC in 304L (UNS S30403) and 316L (UNS S31603) weldments (Ref 57): both austenite and delta ferrite phases may be susceptible; and varying combinations of filler and base materials failed, including matching, higher-, and lower-alloyed filler combinations. Microsegregation of chromium and molybdenum with chemically depleted regions increases susceptibility to localized attack.

Candidate materials for a double hull vessel designed with permanent water ballast, 316L, Nitronic 50 (UNS S20910), and AL6XN (N08367) were evaluated for potential MIC in flowing and stagnant freshwater and seawater (Ref 58). No pitting was observed in AL6XN under any exposure condition after one year. Leaks were located at weld seams of Nitronic 50 and 316L stainless steels after 6 and 8 week exposures to stagnant and flowing seawater. A failed vertical weld in 316 stainless steel after an 8 week exposure to stagnant natural seawater is shown in Fig. 5(a). Figure 5(b) is the corresponding x-ray image indicating failure due to pitting. In all cases, large numbers of bacteria were associated with the corrosion products (Fig. 5c). Residual material in pits was typical of removal of iron. A scanning vibrating electrode technique was used to demonstrate that there were no persistent anodic sites in autogenous welds or heat affected zones of these materials exposed to sterile seawater. The spatial and causal relationship between bacteria and pitting in weldments in 300 series stainless steels is well documented (Ref 59, 60).

Ethylene glycol/water and propylene glycol/water mixtures were evaluated as permanent ballast waters for 316L double hull vessels (Ref 60). The compounds are attractive as ballast liquids because they will have minimal impact if the outer hull is breached and the glycols are released to the environment. Both have low volatility and are miscible with water. In terms of corrosion protection, propylene glycol-based mixtures were shown to protect against pitting of 316L in concentrations of 50% or higher when mixed with seawater (3.5% salinity). Slightly higher concentrations (55%) of ethylene glycol-based mixtures were required under the same conditions to prevent pitting. The compounds have little or no capacity to bind to particulates and will be mobile in soils or sediments. Glycol-based mixtures were also shown to be bacteriostatic at concentrations above 10%. Also, the low octanol/water partition coefficient and measured bioconcentration factors in a few organisms indicate low capacity for bioaccumulation.

Carbon Steel. Unexpectedly rapid localized corrosion of steel bulkheads and ship hull plating of tankers in marine harbor environments was documented (Ref 61). In each case, the localized attack was found beneath macrofouling layers. The biofilm at and around the corrosion sites was

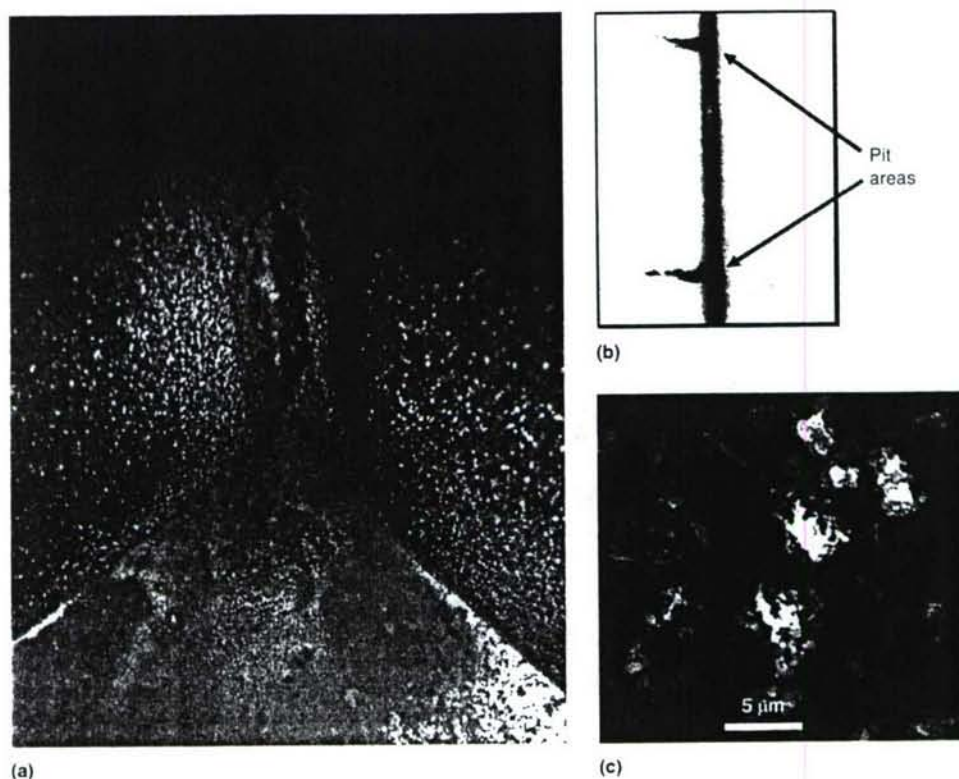


Fig. 5 Vertical weld in 316 stainless steel after exposure to stagnant natural seawater for 8 weeks. (a) Weldment, (b) X-ray of failed vertical weld, (c) Bacteria associated with corrosion products.

populated with a rich consortium of aerobic and anaerobic microorganisms, and the SRB population was elevated by several orders of magnitude above that in the biofilm remote to corrosion sites. Researchers (Ref 62) demonstrated a cycle of sulfur oxidation and reduction causing aggressive corrosion of steel pilings in a harbor. At low tide, the fouling layer was thoroughly aerated and thiobacilli produced oxidized sulfur species. High tide produced anaerobic conditions within the fouling layers and reduction of sulfur compounds.

Natural seawater has also been evaluated as a ballast fluid in unpainted 1020 carbon steel ballast tanks, and deoxygenation has been proposed as a method to reduce corrosion. However, it was determined (Ref 63) that corrosion of 1020 carbon steel coupons in natural seawater over a six month period was more aggressive under stagnant anaerobic conditions than stagnant aerobic conditions as measured by weight loss and instantaneous corrosion rate (polarization resistance) (Fig. 6). Under oxygenated conditions, a two-tiered oxide layer formed (Fig. 7a). The outer oxide layer was reddish-brown and contained numerous filamentous bacteria (Fig. 7b). The inner oxide was extremely adherent and resistant to acid cleaning. Under anaerobic conditions, a nontenacious sulfur-rich corrosion product with enmeshed bacteria formed on carbon steel surfaces (Fig. 7c, d). In anaerobic exposures, corrosion was more aggressive on horizontally oriented coupons compared with vertically oriented coupons. Bulk

water chemistry and microbial populations were measured as a function of time. Both were dynamic despite the stagnant conditions.

Cathodically Protected Carbon Steel. In most cases, carbon steel used in seawater is cathodically protected or painted. It has been reported that cathodic protection retards microbial growth because of the alkaline pH generated at the surface. It was demonstrated (Ref 64) that a potential of -1.10 V SCE markedly decreased settlement of *Balanus cyprids* on painted steel surfaces, but it had no effect on settlement, sand-tube building, reproduction, or larval release of other species. Biofouling in seawater was retarded using pulsed cathodic polarization of steel (Ref 65).

Numerous investigators have demonstrated a relationship between marine fouling and calcareous deposits on cathodically protected surfaces (Ref 66–68); however, their interrelationships are not understood. Microbiological data for cathodically polarized surfaces are often confusing and impossible to compare because of differing experimental conditions (laboratory vs. field) and techniques used to evaluate constituents within the biofilm. Differences in organic content of seawater that produced differences in current density, electrochemistry, calcareous deposits, and biofilm formation have been reported (Ref 66).

The influence of a preexisting biofilm on the formation of calcareous deposits under cathodic protection in natural seawater was studied (Ref 67). It was shown that applied current

densities up to $100 \mu\text{A}/\text{cm}^2$ did not remove attached biofilms from stainless steel surfaces. Both natural marine and laboratory cultures changed the morphology of calcareous deposits formed under cathodic polarization at a current density of $100 \mu\text{A}/\text{cm}^2$.

In one study (Ref 69), cathodic potentials to -1000 mV SCE caused a decrease in pH and an increase of SRB on carbon steel. At potentials more negative than -1000 mV SCE, the pH became more alkaline and SRB numbers decreased. A study of the influence of SRB in marine sediments using electrochemical impedance spectroscopy to monitor corrosion and lipid analysis as biological markers, complemented by chemical and microbiological analysis, showed that -880 mV SCE encouraged the growth of hydrogenase-positive bacteria in the sediment surrounding the metal and facilitated the growth of other SRB species (Ref 70).

Because the enumeration technique strongly influences the number of cells one is able to count, and because the number of cells cannot be equated to cellular activity, including sulfate reduction, some investigators have attempted to measure cellular activity directly on cathodically protected surfaces. One investigator (Ref 71) cathodically protected 50D mild steel (BS 4360) coupons exposed in the estuarine waters of Aberdeen Harbor using an imposed potential of -950 mV Cu:CuSO₄ and sacrificial anodes. Activities within biofilms were determined using a radiorespirometric method—a technique for studying microbial respiration using

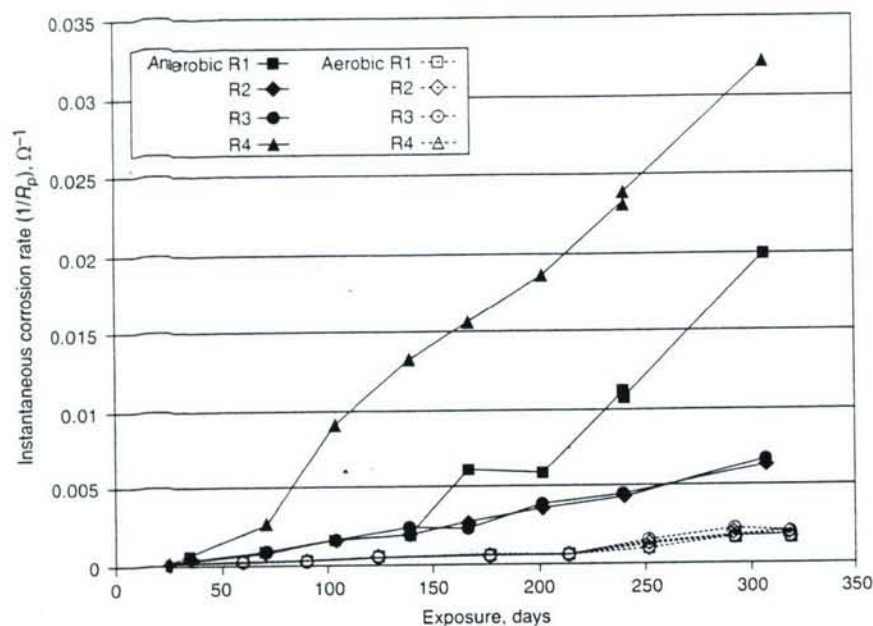


Fig. 6 Instantaneous corrosion rates using polarization resistance (R_p) for carbon steel exposed in stagnant aerobic or stagnant anaerobic natural seawater. Corrosion rates were higher for the anaerobic exposures (solid lines) than for aerobic exposure (broken lines). R1, R2, R3, and R4 refer to the vertical location of the electrode, with R1 being closest to the water surface and R4 located at the bottom of the experimental chamber.

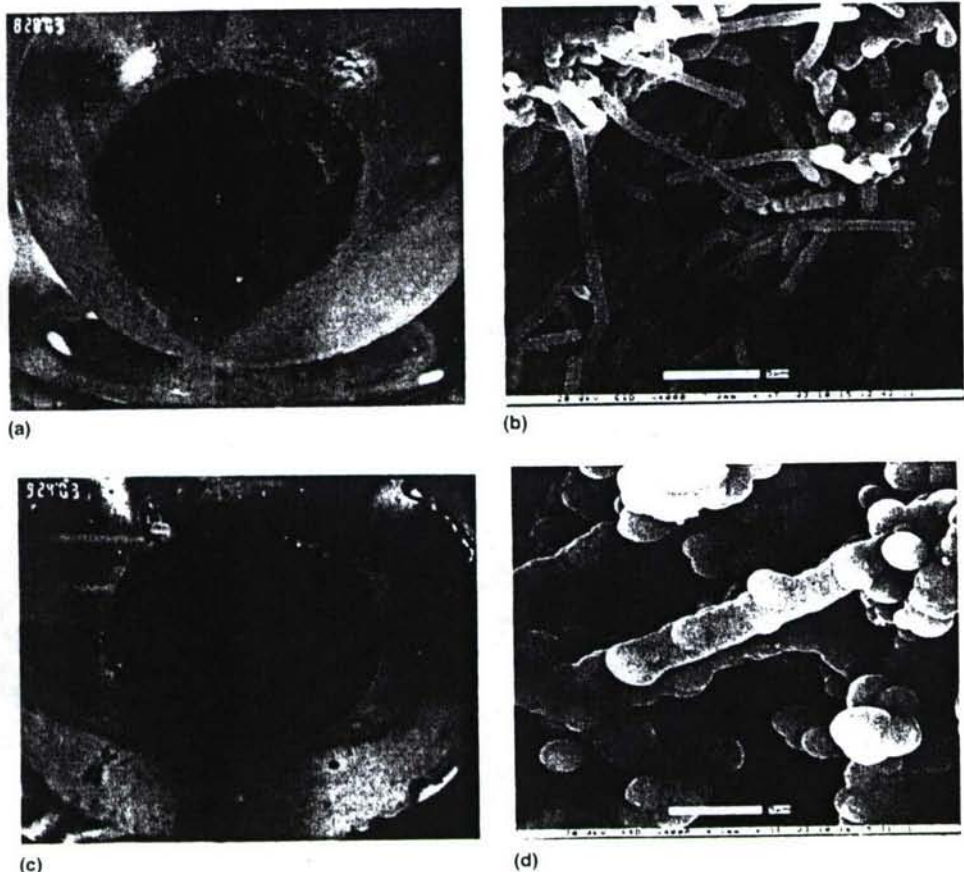


Fig. 7 Carbon steel electrodes exposed to aerobic and anaerobic natural seawater for 290 days. (a) Aerobic. (b) Aerobic. Scanning electron micrograph of iron-oxide encrusted bacteria enmeshed in corrosion products. (c) Anaerobic. (d) Anaerobic. Scanning electron micrograph of sulfide-encrusted organisms enmeshed in corrosion products.

radiolabeled substrates or electron acceptors. Biofilms developed on all substrata—both unprotected and cathodically protected surfaces. The activities of aerobic and anaerobic bacteria, including SRB, were significantly greater on unprotected coupons. Furthermore, sulfide, a metabolic fingerprint of SRB activity, could be detected only in biofilms on unprotected coupons. These results show that a potential of $-950 \text{ mV Cu:CuSO}_4$ does not prevent SRB from developing on cathodically protected surfaces. The lower activity of SRB within biofilms on cathodically protected coupons was not directly caused by any inhibitory effect of the cathodic potential. Instead, the greater activity of SRB on unprotected coupons was the result of production of an extensive corrosion film offering more favorable anaerobic conditions.

The NACE Standard (Ref 72), which is currently under revision, lists cathodic protection criteria for underground or submerged steel, cast iron, aluminum, and copper structures. Microbiologically influenced corrosion is cited as "one of several abnormal conditions which sometimes exist and where cathodic protection is ineffective or only partially effective." It is important to point out that in several studies (Ref 66–68), SRB were present on cathodically protected steels, but accelerated corrosion was not reported.

Thermodynamic data with iron in a pH 7 electrolyte saturated with hydrogen sulfide was studied (Ref 73). A potential of -1024 mV SCE was required to achieve cathodic protection. It was demonstrated (Ref 74) that -1024 mV was capable of providing cathodic protection in the presence of active SRB. The influence of cathodic protection on the growth of SRB and on corrosion of steel in marine sediments was investigated (Ref 75). The investigators concluded that a cathodic potential of -880 mV SCE did not appear to be sufficient for protection and that large amounts of cathodically produced hydrogen promoted the growth of SRB in the sediments surrounding the samples. Laboratory tests were conducted (Ref 76) in anaerobic, artificial sediments containing SRB. Results indicated that a polarization of -1024 mV SCE was adequate for corrosion protection. Cathodic protection current density was between 4.5 and 12 mA/ft^2 . Another study (Ref 77) indicated that a cathodic potential of -1054 mV SCE lowered the corrosion rate of steel by 82.7% , even though protective potentials in the range -774 to -1134 mV SCE did not inhibit growth of SRB. It was concluded (Ref 78) that if anaerobic bacterial activity is suspected, a cathodic polarization shift of approximately 200 to 300 mV SCE is required for carbon steel protection. Cathodic protection was imposed on steel surfaces actively corroding in cultures of SRB (Ref 79), and it was concluded that cathodic protection in the presence of SRB decreased corrosion by a factor of 8 or 9 .

It was shown (Ref 80) that cathodically protected stainless steel surfaces in artificial seawater can become colonized by aerobic,

acid-producing bacteria. Formation of calcareous deposits and initial settlement of microorganisms resulted in decreased current density requirements to maintain a protection potential. Subsequent colonization and pH changes destabilized the calcareous deposits and dramatically increased the current density required to maintain the protected potential.

Hydrogen embrittlement of carbon steel is a form of corrosion involving the cathodic reaction. Atomic hydrogen generated in the cathodic reaction penetrates the steel resulting in the loss of ductility. A number of mechanisms have been postulated to account for the embrittlement effect, which, when combined with the presence of local regions of high stress, can result in severe cracking (Ref 81). Hydrogen embrittlement is enhanced by the high levels of hydrogen generated by SRB under certain conditions, as well as that generated by overly aggressive cathodic protection systems. If the levels of cathodic protection are increased too high to combat SRB corrosion, there is a danger that hydrogen embrittlement may be enhanced. The presence of H_2S , which can be produced by SRB, is known to retard formation of molecular hydrogen on the metal surface and to enhance adsorption of atomic hydrogen by the metal. Whenever algae provide conditions for SRB, they may also enhance hydrogen embrittlement.

In summary, bacteria can settle on cathodically protected surfaces. Cathodic potentials to -1074 mV SCE do not prevent biofilm formation. It has been suggested that actual cell numbers may be related to polarization potential, dissolved organic carbon, or to the enumeration technique. Numbers of SRB may be increased or decreased depending on exposure conditions. Carbon steel is considered protected when a potential of -924 mV SCE is achieved. In many cases, the potential is further reduced to -1024 mV SCE to protect the steel from corrosion caused from the activity of SRB. The decreased potential is not applied to prevent growth of SRB but is based on a theoretical level that will allow passivity of steel in a sulfide-rich environment produced by SRB. The main consequence of biofilm formation on protected surfaces appears to be an increase in the current density necessary to polarize the metal to the protected potential. The presence of large numbers of cells on cathodically protected surfaces does mean that in the event that cathodic protection is intermittent, discontinuous, or discontinued, the corrosion attack due to the microorganisms will be more aggressive.

Coated Carbon Steel. Although coatings alone do not prevent MIC, they delay the onset of MIC and other corrosion reactions. Many types of polymeric coatings can be subject to biodegradation. The attack is usually caused by acids or enzymes produced by bacteria or fungi. This often results in selective attack on one or more specific components of a coating system with consequent increase in porosity and water or other ion transport through the coating and the formation of blisters, breaches, and disbanded

areas. Many of these effects have recently been reviewed (Ref 82). It was also demonstrated (Ref 83) that marine bacteria are attracted to corrosion products at coating defects. The microorganisms responsible for damage to coatings may or may not be involved in corrosion initiation under the damaged coating.

Titanium and Titanium Alloys. There are no case histories of MIC for titanium and its alloys. One investigator (Ref 84) reviewed mechanisms for MIC and titanium's corrosion behavior under a broad range of conditions. He concluded that at temperatures below $100^\circ C$ ($212^\circ F$) titanium is not vulnerable to iron/sulfur-oxidizing bacteria, SRB, acid-producing bacteria, differential aeration cells, chloride concentration cells, and hydrogen embrittlement. In laboratory studies, (Ref 85) corrosion of Grade 2 titanium (UNS 850400) was not observed in the presence of SRB or iron/sulfur-oxidizing bacteria at mesophilic ($23^\circ C$, or $73^\circ F$) or thermophilic ($70^\circ C$, or $158^\circ F$) temperatures. Using the model in Ref 86, one would predict that titanium would be immune to SRB-induced corrosion. There are no standard free energy reaction data for the formation of a titanium sulfide. If one assumes a hypothetical sulfide product to be titanium sulfide, the standard enthalpy of reaction is $+587$ kJ. While standard free energies of reaction are not identical to standard enthalpies of reaction, it is still unlikely that titanium will be converted to the sulfide under standard conditions of temperature and pressure.

Aluminum alloys were evaluated (Ref 87) for the impact of microorganisms on corrosion of aircraft in bilge and toilet areas. The researchers isolated numerous microbiological species and were able to cause corrosion of 7075, which is used in aircraft construction. However, the authors could not relate their experiments to actual aircraft.

Polymeric Composites. Microorganisms and their products can be responsible for changes in physical, chemical, and electrochemical properties of polymeric materials. Reference 88 demonstrated that under immersion conditions, epoxy and nylon coatings on steel were breached by mixed cultures of marine bacteria.

In laboratory experiments (Ref 89), it was demonstrated that epoxy resin and carbon fibers, either individually or in composite, were not degraded by sulfur/iron-oxidizing, hydrogen-producing, calcareous depositing, or SRB. Bacteria colonized resins, fibers, and composites but did not cause damage. Sulfate-reducing bacteria preferentially colonized vinyl ester composites at the fiber-resin interfaces, and hydrogen-producing bacteria appeared to disrupt the fiber-vinyl ester resin bonding with penetration of the vinyl ester resin.

It is standard practice to coat the surface of the filaments with a sizing chemical to provide a better bonding with the resin matrix and to prevent abrasion between individual fibers during shipping and handling. This treatment permits optimal stress transmission between filaments. Fiber sizing chemicals are starch-oil mixtures.

The sizing materials are highly susceptible to biodegradation of strength resulting from abrasion between fibers and as a coupling agent to the matrix. The sizing materials are highly susceptible to biodegradation and can be expected to decompose in the presence of contaminating microorganisms (Ref 90).

Researchers (Ref 91, 92) investigated fungal degradation of polyimides used as insulators in electronic packaging. Growth of microorganisms on these polymers was found to result in loss of their dielectric properties. They also studied biodeterioration of fiber-reinforced composites, graphite sheets, and graphite fibers used in composite materials. They observed fungal penetration into composite resin and graphite sheets and concluded that fungi caused substantial damage to composites under conditions favorable to fungal growth. Investigators (Ref 93) demonstrated in the laboratory that mixed cultures of marine bacteria could penetrate three conductive caulks (PRC 1764, PI8500, and PI8505) used to secure antenna foundations to ship superstructures.

Burial Environments

Tapes and coatings for buried pipes and cables are susceptible to biodegradation and MIC (Ref 94). A recent study evaluated the potential for MIC of unexploded ordnances (UXO) buried in soil environments. Unexploded ordnances are military munitions that have been prepared for action but remain unexploded and constitute a potential hazard. The 1998 Defense Science Board estimated 1,400 individual sites contained UXO (Ref 95). The munitions corrode at varying site-specific corrosion rates. In most subsurface environments, microbial growth is limited by water. The likelihood that MIC will take place is directly related to water availability. Microorganisms concentrate at interfaces, including soil/surface interfaces. A survey determined that the microbial populations measured on the surface of UXO were sufficient to cause localized corrosion and that the most likely mechanism was microbial acid production. Microbially induced corrosion of carbon steel is independent of pH over pH values 4.5 to 9.5. In this range, the corrosion products maintain a pH of 9.5 next to the steel surface, regardless of the pH of the solution. At a pH of 4 or below, hydrogen evolution begins and corrosion increases rapidly. Fungi and acid-producing bacteria can reduce the pH locally to values below 4.0. The localized corrosion mechanism of the steel fragments was in many cases pitting, with pits inside pits, indicating multiple initiation sites. In other cases, tunneling was observed. Both types of localized corrosion are consistent with microbiological acid-induced corrosion.

ACKNOWLEDGMENT

Preparation of this chapter was funded under Office of Naval Research Program Element

0601153N, Work Unit No. 5052, NRL/BC/7303/04/0001.

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